chlorocyano- and bromocyanobenzenes, this procedure was not completely clear-cut, and assignment was made so as to give the most consistent results with the remainder of the data in Table I and earlier work (*3*).

Chemical shifts were also determined for 1,2-dimethoxybenzene (a single line in carbon tetrachloride), 1,2-dinitrobenzene, and 1,2-dicyanobenzene. The latter two gave typical AA′BB′ spectra, which were analyzed only for chemical shifts by oft published procedures. The results are given also in Table I.

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Vapor-Liquid Equilibria of Binary Systems Containing Alcohols

Methanol with Aliphatic Amines

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Vapor-liquid equilibrium data are reported for three binary systems of methanol with *n*-butylamine ($BuNH_2$), diethylamine (Et_2NH), and triethylamine (Et_3N) at 730 mm. of Hg. As expected from a strong hydrogen-bond interaction between hydroxyl group and amino bases, both the methanol-$BuNH_2$ and methanol-Et_2NH systems show negative deviation from Raoult's law. However, the methanol-Et_3N system shows a positive deviation and no azeotrope can be found. Et_2NH forms an azeotropic mixture at 67.2° C. near 76.0 mole % of methanol, while a tangent azeotrope seems to occur in methanol-$BuNH_2$.

VAPOR-LIQUID equilibrium data of alcohol-amine systems are of theoretical and practical importance. A review of the literature indicates that no isobaric equilibrium data are available for binary systems of methanol with aliphatic amines, except for some information on the azeotropic behavior (*5*). This paper deals with the isobaric vapor-liquid equilibrium data of three binary systems of methanol with *n*-butylamine, diethylamine, and triethylamine.

EXPERIMENTAL

The sample liquids used in this study were prepared by the procedure described in the previous paper (*8*). Table I lists some physical properties of the final purified samples

Table I. Physical Properties of Purified Liquids and the Antoine Constants Used

	Methanol	$BuNH_2$	Et_2NH	Et_3N
Boiling point, *t*, ° C.				
Obsd.	64.8	78.0	55.4	89.4
Lit.[a]	64.5 ~ 7	77.8	55.5	89.5
Density, d_{25}^{4}				
Obsd.	0.78653	0.73514	0.69893	0.72353
Lit.[a]	0.7866	0.7369	0.6926	0.7235
Refractive index, n_D^{25}				
Obsd.	1.3265	1.3972	1.3824	1.3979
Lit.[a]	1.3267	1.4004	1.3783	1.3980
Antoine constants[a,b]				
A	8.07246	7.2130	7.14099	7.18658
B	1574.99	1308.4	1209.9	1341.3
C	238.86	224.2	229.0	222.0

[a] Reference (*3*). [b] Reference (*6*).

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as well as the Antoine constants used for calculating the vapor pressure of component liquids.

The vapor-liquid equilibrium data were determined on a modified Colburn still used in the previous study (*8*). The amine-alcohol mixtures are somewhat unstable when heated in presence of oxygen. Therefore the equilibrium still was blanketed with nitrogen except for the methanol-$BuNH_2$ system. The compositions of the equilibrium sam-

Table II. Vapor-Liquid Equilibrium Data at 730 Mm. of Hg

Methanol Concentration, Mole %		Temp.,[a] ° C.	Activity Coefficients, γ	
Liquid	Vapor		Methanol	Amine
		Methanol-*n*-Butylamine		
3.6	3.2	...	...	...
9.4	11.3	...	...	...
28.0	27.9	77.5	0.614	1.014
34.9	37.7	77.4	0.667	0.971
55.6	63.5	75.6	0.754	0.887
65.5	75.2	74.1	0.802	0.817
69.0	79.6	73.7	0.818	0.758
71.0	81.0	72.7	0.840	0.781
72.0	82.8	72.1	0.864	0.746
78.1	88.8	71.3	0.882	0.640
87.0	97.5	67.7	0.995	0.272
		Methanol-Diethylamine		
16.9	9.4	57.4	0.749	1.006
19.2	10.8	57.9	0.740	0.999
25.8	14.7	59.1	0.715	1.001
26.8	15.3	59.2	0.715	1.002
35.5	22.2	61.0	0.726	0.985
45.3	31.4	62.7	0.750	0.967
49.2	36.8	63.6	0.783	0.933
58.9	50.1	65.3	0.830	0.860
60.0	51.5	65.6	0.827	0.850
66.0	59.9	66.5	0.845	0.804
67.4	62.3	66.8	0.851	0.781
67.9	62.3	66.7	0.848	0.795
68.0	63.9	66.9	0.862	0.759
71.9	70.0	66.9	0.892	0.718
73.6	71.8	...	...	...
75.8	75.5	67.3	0.899	0.672
78.1	79.1	67.1	0.920	0.637
78.2	78.3	67.0	0.916	0.669
79.9	81.2	67.1	0.924	0.625
83.6	85.7	67.0	0.938	0.586
87.4	89.3	...	...	...
94.3	96.4	65.7	0.983	0.442
97.4	98.4	...	...	...
		Methanol-Triethylamine		
5.3	20.8	83.1	1.977	1.032
12.6	36.1	78.0	1.731	1.073
18.9	43.5	75.2	1.541	1.127
22.7	47.6	74.0	1.468	1.144
28.5	53.5	72.5	1.391	1.159
37.1	59.1	70.7	1.263	1.235
41.7	63.7	69.8	1.254	1.223
47.5	66.0	69.2	1.168	1.301
54.0	69.9	68.4	1.122	1.353
58.3	71.8	68.0	1.084	1.419
62.3	74.4	67.5	1.072	1.452
65.9	75.8	67.2	1.045	1.535
72.6	80.2	66.6	1.027	1.598
77.7	83.3	66.1	1.013	1.682
83.1	86.6	65.7	1.003	1.813
87.9	90.0	65.3	0.999	1.914
91.9	93.5	65.0	1.007	1.885
96.2	96.6	64.7	1.004	2.122

[a] Corrected to 760 mm. of Hg.

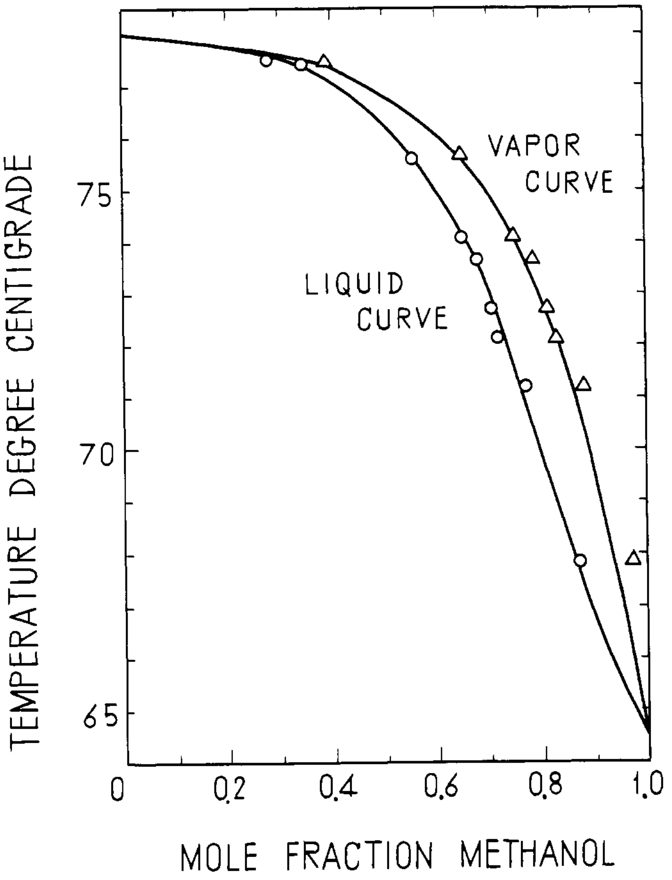

Figure 1. Vapor-liquid equilibrium diagram for the methanol–*n*-butylamine system

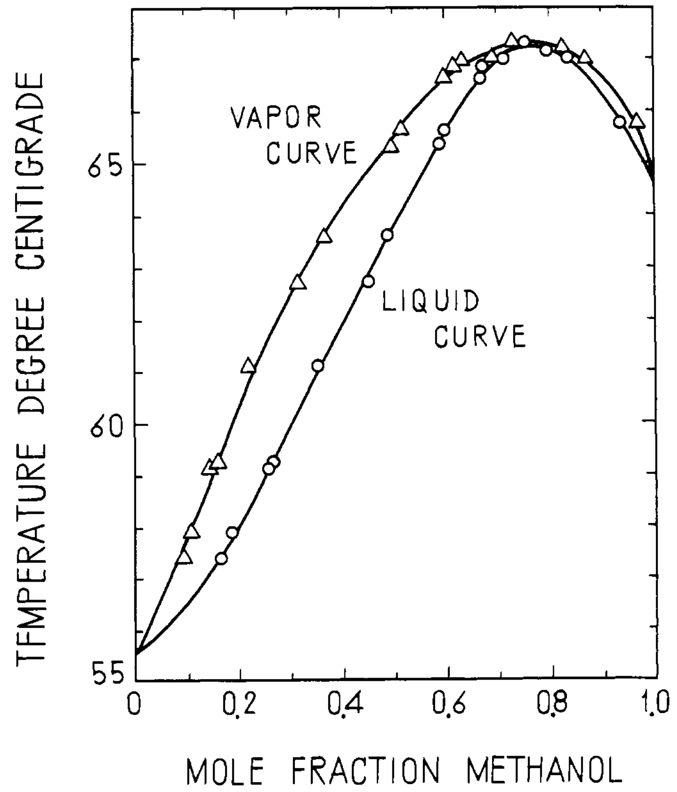

Figure 2. Vapor-liquid equilibrium diagram for the methanol-diethylamine system

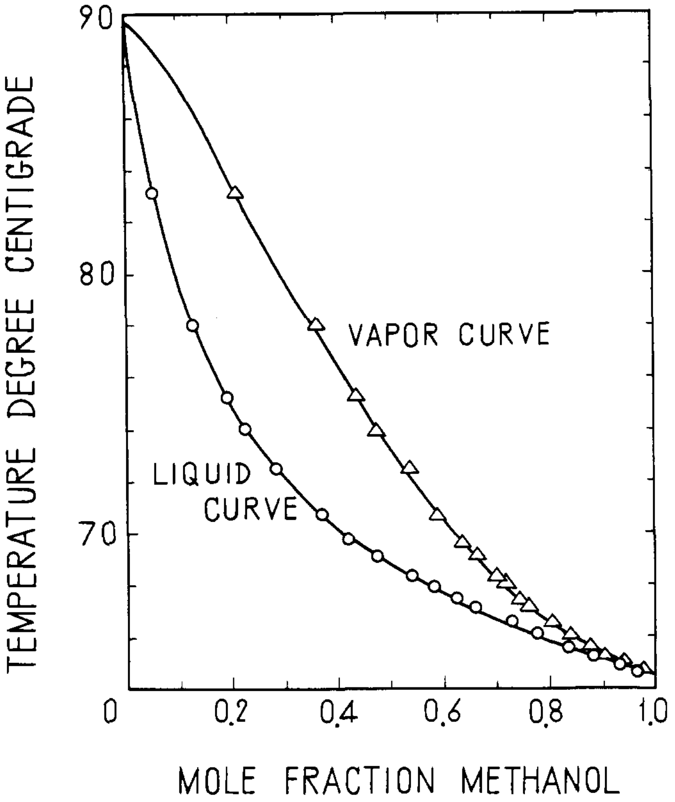

Figure 3. Vapor-liquid equilibrium diagram for the methanol-triethylamine system

ples were determined by density measurement at 25° C. (*7*) using a bicapillary-type pycnometer. Experimental errors in the temperature and composition determination were estimated to be less than ±0.1° C. and ±0.15 mole % of methanol, respectively.

RESULTS AND DISCUSSION

Table II lists the data obtained in this work. The measurements were performed at a mean pressure of 730 mm. of Hg and the temperature was corrected to the normal boiling point.

The activity coefficients γ were calculated by the equation

$$\gamma = \frac{y\pi}{xp} \tag{1}$$

where the assumption of the perfect gas law and the gas phase and the neglect of the volume of the liquid phase are involved. The maximum boiling point differences between pure liquids are less than 25° C. and the reduced temperature t_R ($t_R = t/t_C$, where t_C is the critical temperature) for both components falls between 0.33 and 0.23. Under these conditions, the correction factor due to the vapor phase imperfection was negligible.

As the *t-x-y* diagrams in Figures 1 to 3 illustrate, the maximum boiling azeotrope in the methanol-diethylamine system occurs at 67.2° C. and consists of 0.76 mole fraction of methanol. The azeotropic temperature found in this study is in accord with the literature value (*5*), 66.2° C. at 740 mm. of Hg, but the azeotropic composition differs appreciably from the literature value (*5*) of 0.60. The methanol-*n*-butylamine system seems to be a tangent azeotrope at an infinite dilution of methanol. The methanol-triethylamine system is, on the contrary, a nonazeotropic system. The same result was cited by Horsley (*5*).

Table III. Margules Constants Evaluated and the Fitness of the Margules Equation

	MA	MB	MC	$1/n$ $\Sigma(\gamma_{\text{Obsd.}} - \gamma_{\text{Calcd.}})^2$ [a]
Methanol-BuNH$_2$	−0.10	−0.48	...	0.00467
Methanol-Et$_2$NH	−0.091	−0.435	+0.052	0.00059
Methanol-Et$_3$N	+0.37	+0.32	...	0.00697

[a] n = Number of experimental points.

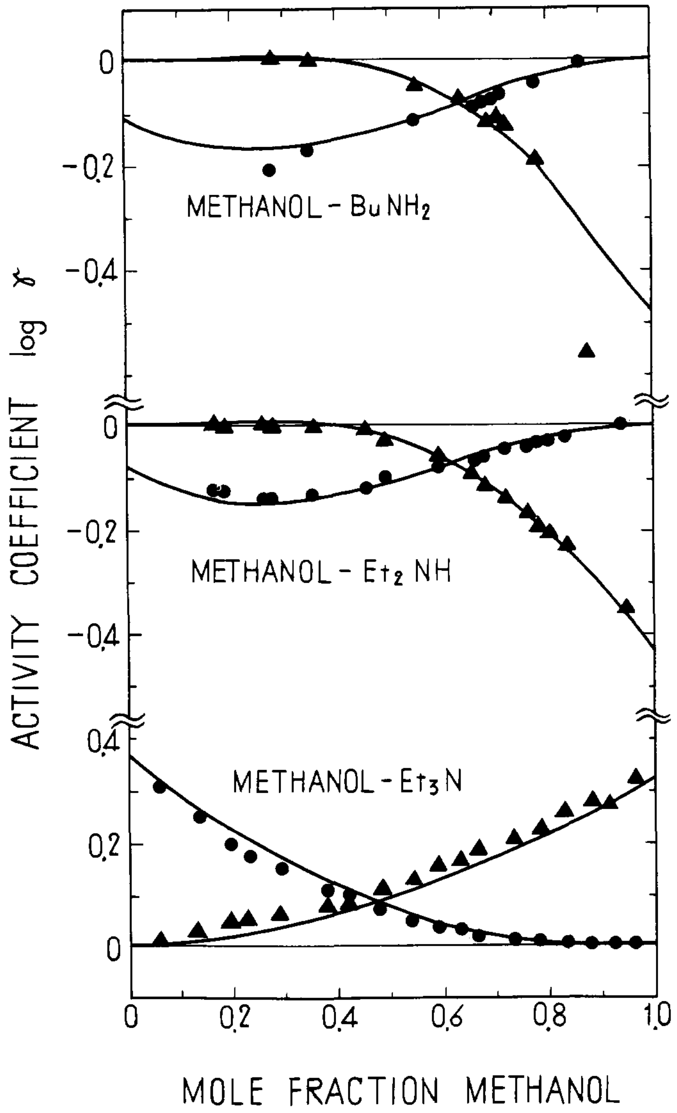

Figure 4. Diagram of activity coefficients vs. composition

As for the thermodynamic consistency test proposed by Redlich and Kister (*9*) and supplemented by Herington (*4*), the data for methanol-*n*-butylamine and -diethylamine systems were reasonable but those for methanol-triethylamine were less satisfactory.

Evidently, the present data show that the activity coefficient of methanol takes minima in *n*-butylamine and diethylamine, and therefore, the van Laar type of equation will fail to fit the data. Thus the Margules type of equation was used for correlation. The data can be correlated fairly well by the two-constant Margules equation

$$\left.\begin{array}{l} \log \gamma_1 = x_2^2[MA + 2(MB - MA)x_1] \\ \log \gamma_2 = x_1^2[MB + 2(MA - MB)x_2] \end{array}\right\} \tag{2}$$

where subscript 1 refers to methanol. For the methanol-diethylamine system, the three-constant Margules equation derived from the general expression for the excess free energy of mixing (*10*) was used. If we denote the third constant, in addition to two constants, *MA* and *MB* in Equation 2, as *MC*, the equation can be written as

$$\left.\begin{aligned}\log \gamma_1 &= x_2^2[MA - 2(MA - MB + MC)x_1 + 3MC(x_1)^2]\\ \log \gamma_2 &= x_1^2[MB - 2(MB - MA + MC)x_2 + 3MC(x_2)^2]\end{aligned}\right\} \quad (3)$$

A set of the Margules constants was evaluated from the data and tabulated in Table III. The sum of square of the deviation of calculated γ value from experimental one is given in the same table. The experimental and calculated γ values by Equation 2 or Equation 3 (for methanol-diethylamine system) are plotted in Figure 4. The correlation is especially satisfactory for the methanol-diethylamine system.

CONCLUSIONS

The present data indicate that the negative deviation from the ideal solution law are observed for the methanol-*n*-butylamine and methanol-diethylamine systems and that the methanol-triethylamine system shows, contrary to our expectation, a positive deviation which seems to be attributed to a sort of steric interference. These results are in harmony with those reported by Copp (*1*, *2*).

NOMENCLATURE

MA, MB, MC = Margules constants
p = vapor pressure, mm. of Hg
x, y = composition of liquid and vapor, mole fraction, respectively
γ = activity coefficients
π = total pressure, mm. of Hg

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Proton Magnetic Resonance Spectra of Malonate Esters

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The NMR spectra of a number of open chain and cyclic malonic esters have been measured and the characteristic resonances for the various protons in such molecules established.

IN CONNECTION with our studies on the stereochemistry of the addition of diethyl malonate to 4-*tert*-butyl-1-cyanocyclohexene (*5*) it was important to make assignments to individual protons in the NMR spectra of the malonate esters obtained. Until that time, there were no reported studies on the NMR spectra of malonate esters, but since then the spectra of diethyl malonate (*11*) and of esters of alkoxymethyl ethylmalonic acids (*10*) have been described. The spectra of some acyclic and cyclic malonate esters are now discussed.

EXPERIMENTAL

Most of the esters were commercially available and were purified before use. Diethyl ethyldeuteromalonate was prepared from the sodium salt of the ester (*1*), diethyl cyclohexylmalonate was made using the method of Hope and Perkin (*7*), and dimethyl 3-α-cholestanylmalonate and dimethyl 3-β-cholest-5-enylmalonate were obtained from the corresponding tosylates and sodiomalonic ester (*9*). Isopropylidene ethylmalonate and isopropylidene dimethylmalonate were available from a previous study (*2*). Diethyl β-cyanoethylmalonate (*6*) and diethyl 2-cyanopropylmalonate (*4*) were prepared by standard cyanoethylation reactions.

The NMR spectra were measured on a Varian A 60 instrument, tetramethylsilane being the internal standard, and CCl_4 was used as solvent except as specified. The results are summarized in Tables I and II in which only characteristic peaks are listed.

RESULTS AND DISCUSSION

The assignments for the ester CH_2 groups and for the α-CH groups are, in most cases, clear-cut. The former give rise to a 4H quartet, usually around 5.85 τ(J = 7 c.p.s.). As expected, methyl esters absorb at a somewhat higher field. The doublet observed for dimethyl 3-β-cholest-5-enylmalonate is probably due to the two ester functions in the equatorial malonate being in different magnetic environments, one of them coming under the influence of the anisotropic effect of the olefinic double bond. The slight